



Research on Selected Types of Lustrous Carbon Carriers After the High-Temperature Pyrolysis

J. Kamińska^{a,*}, M. Stachowicz^b, M. Kubecki^c

^a Łukasiewicz Research Network – Krakow Institute of Technology, Poland

^b Wrocław University of Technology, Faculty of Mechanical Engineering, Poland

^c Łukasiewicz Research Network – Institute for Ferrous Metallurgy, Gliwice, Poland

* Corresponding author: Email address: jadwiga.kaminska@kit.lukasiewicz.gov.pl

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Abstract

For research purposes and to demonstrate the differences between materials obtained from the carbonaceous additives to classic green moulding sands, five lustrous carbon carriers available on the market were selected. The following carbonaceous additives were tested: two coal dusts (CD1 and CD2), two hydrocarbon resins (HR1 and HR2) and amorphous graphite (AG1). The studies of products and material effects resulting from the high-temperature pyrolysis of lustrous carbon carriers were focused on determining the tendency to gas evolution, including harmful compounds from the BTEX group (benzene, toluene, ethylbenzene and xylene). Moreover, the content of lustrous carbon (LC), the content of volatile matter and loss on ignition (LOI) of the carbonaceous additives were tested. The solid products formed during high-temperature pyrolysis were used for the quantitative and qualitative evaluation of elemental composition after the exposure to temperatures of 875°C in a protective atmosphere and 950°C in an oxidizing atmosphere. The conducted studies have indicated the necessity to examine the additives to classic green moulding sands, which is of particular importance for the processing, rebonding and storage of waste sand. The studies have also revealed some differences in the quantitative and qualitative composition of elements introduced to classic moulding sands together with the carbonaceous additives that are lustrous carbon carriers. It was also considered necessary to conduct a research on lustrous carbon carriers for their proper and environmentally friendly use in the widely propagated technology of classic green sand system.

Keywords: Foundry, Green moulding sand, Lustrous carbon, Pyrolysis, Core shooting

1. Introduction

Despite the fact that there are many new and more advanced casting technologies, sand casting remains one of the most widely used casting processes. This is due to the low cost of raw materials, the possibility of making a wide range of castings in terms of their size and the possibility of the used sand reclamation [1, 2].

Most of the iron castings produced in the European Union are made in classic green moulding sands (Fig. 1). Apart from the base sand, the main components of these mixtures are bentonite and a lustrous carbon carrier [3-5]. The most popular carbonaceous additive is still coal dust. The positive effect of coal dust on the quality of the outer surface of iron castings has been known since the 18th century [6, 7]. Classic green moulding sands with bentonite are considered to be one of the most ecological sand mixtures, but the addition of carbon carriers, like coal dust or

synthetic resins, makes them harmful to the natural environment [8-10].

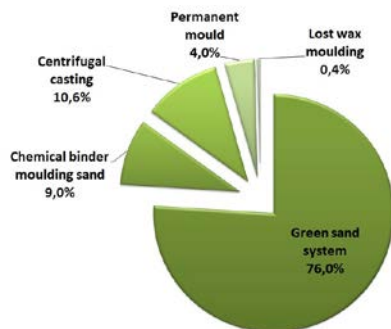


Fig. 1. Share of green sand system in moulding techniques [4]

After pouring the mould with liquid metal, in particular with iron alloys, during the pyrolysis of high-temperature carbonaceous additives leading to the formation of lustrous carbon, volatile organic compounds (VOCs) are released, including hazardous air pollutants (HAPs), whose chemical composition includes numerous organic compounds such as PAHs (polycyclic aromatic hydrocarbons) and BTEX (benzene, toluene, ethylbenzene, xylene). They are particularly harmful because of their carcinogenic, mutagenic and teratogenic effects [11].

There is a lot of information in the literature on the types of lustrous carbon carriers used for classic moulding sands. Lewandowski and Holtzer [5, 6, 12] described the types of lustrous carbon carriers and the possibility of eliminating coal dust from classic moulding sands by replacing the coal dust with other organic compounds and carbonaceous additives. Apart from ecological aspects, one of the reasons to search for other carriers of lustrous carbon is the occurrence of surface defects in iron alloy castings, caused in particular by the addition of coal dust [13,14,15]. In other publications [9, 16, 17, 18], the authors focused on determining the influence of coal dust and hydrocarbon resins on the toxicity of classic moulding sands. Stefański and Engelhardt [19, 17] described coal dust substitutes with increased ability to create lustrous carbon, which enables reducing their quantity in moulding sand. In other researches on the possibility of reducing/eliminating additives based on coal dust, the use of cellulose was discussed [20, 21].

Another aspect of the use of lustrous carbon carriers includes residues of the high-temperature pyrolysis of carbon additives [22]. The studies of the problem [23] indicate possible risk of acidification and salinity of the system sand, which reduces the sand binding capacity. Moreover, tests of the waste system sands [24] stored in landfills show concentration of the following metals: As, Ba, Cd, Cr, Pb, Hg, Se, Ag, Cu and Zn.

2. Purpose and scope of the research

To study and compare the materials after the high-temperature pyrolysis obtained from the carbonaceous additives to classic moulding sands, five potential lustrous carbon carriers (LC) were selected (Table 1), i.e. two hydrocarbon resins (HR1 and HR2),

two coal dusts (CD1 and CD2) and amorphous graphite (AG1). The comparison of the material effects resulting from the high-temperature pyrolysis of coal dust and lustrous carbon carriers, including the evolution of gases and solids formed, was based on the following tests: lustrous carbon content (LC), loss on ignition (LOI), volatile matter content, extensive gas formation tests and analysis of the elemental composition of the residues after the exposure to temperatures of 875°C and 950°C. The qualitative and quantitative determination of elements introduced to the sand mixture together with the carbonaceous additives is of particular importance for the processing, rebonding and storing of waste sands.

Table 1.

Properties of carbonaceous additives potentially used as an additive to the green sand system

Carrier number and designation used in the article	Type of lustrous carbon carrier	Country of origin	Water content in as-delivered condition %
No. 1/HR1	hydrocarbon resin	Estonia (E)	0.15
No. 2/HR2	hydrocarbon resin	Germany (G)	0.12
No. 3/CD1	coal dust	Czech Republic (CR)	0.15
No. 4/CD2	coal dust	Russia (R)	0.16
No. 5/AG1	amorphous graphite	Austria (A)	0.18

The loss on ignition test (LOI), involving heating of the previously dried sand sample, was carried out in a high-temperature chamber furnace, model FCF 4/160M, made by CZYLOK at a temperature of 950°C for a period of 2 hours (according to PN-83/H04119), followed by cooling down and weighing on the OHAUS EX324M laboratory scale with an accuracy of 0.0001 g.

The volatile matter content characterizes the degree of thermal decomposition of the organic matter present in coal. The volatile matter content was determined in accordance with the recommendations of the PN-G-04516 standard at a temperature of 875°C for 420 s in an atmosphere protecting the sample against oxidation. In the study, 1 g of the carbonaceous additive was used.

The amount of emitted gases (gas-forming tendency) was determined in accordance with the industrial standard BN-76/4024-05. The measurement was carried out in an electric furnace provided with a temperature control unit in a measuring range of up to 1300°C. The measurement consisted in placing the measuring boat with the sample put inside in a furnace heated to 1000°C. For the measurement of gas-forming tendency, 1 g of dried material was placed in the boat. The volume of emitted gases was read every 5 seconds. The test was designed to end after 500 s. The end time of the test corresponded to the volume of gases in the burette which did not undergo any further changes.

The studies of materials after the high-temperature pyrolysis were supported with images taken on a Hitachi TM-3000 scanning microscope with an attachment for the X-ray energy

dispersive spectrometry (EDX) supplied by Oxford Instruments to carry out the quantitative and qualitative analysis of elements.

3. Results

Table 2 summarizes the results of the determination of basic indicators used in the quality assessment of carbonaceous additives introduced to classic moulding sands to obtain a coating on the sand grains produced by the lustrous carbon (LC). The results of gas activity tests for all five tested: coal dusts and lustrous carbon carriers are presented in Figure 2.

Table 2.

The results of tests of carbonaceous additives as a lustrous carbon (LC) carriers

Carrier number/designation	Loss on ignition LOI, %	Volatile matter content, %	Lustrous carbon content LC, %
No. 1/HR1	99.975	92.724	55.30
No. 2/HR2	99.998	90.173	45.44
No. 3/CD1	96.606	33.697	9.35
No. 4/CD2	93.033	54.198	6.83
No. 5/AG1	92.827	3.631	0.25

The averaged values of the examined indicators presented in Table 2, which are also the quality criteria of commercially available carbonaceous additives, highlight the course of action when selecting the appropriate lustrous carbon carrier for the classic green sand system. Studies of the LC index (%) clearly indicate the usefulness of hydrocarbon resins No. 1/HR1 and No. 2/HR2, which confirms the earlier research on this kind of additive carried out by D. Kwaśniewska-Królikowska et al. [3]. At a given temperature of the pyrolysis process (875°C), they have 5 times greater ability to form lustrous carbon (LC) than coal dust No. 3/CD1 and about 220 times greater ability than amorphous graphite No. 5/AG1.

Another examined criterion for the evaluation of coal dusts, amorphous graphite and hydrocarbon resins is their gas-forming tendency (Fig. 2), which is important in the aspect of the occurrence of a specific group of defects in castings, i.e. gas porosity, especially in iron casts [25] made in classic green moulding sands (excessive gas formation means gas defects in castings).

In all tested carbonaceous additives, the stabilization of gas volume in the burette of the measuring device allowed the measurement to be terminated after 80 s. Among the tested carbon bearing materials, only No. 5/AG1 differed from other materials in its low gas-forming activity of 28 cm³/g. The remaining lustrous carbon carriers as additives to the green sand system have reached the gas activity of >250 cm³/g as early as after 40 s from the start of the measurement. Analysing Figure 2, the difference in the volume of the gas released is clearly visible starting with the 15th second of the measurement, when comparing the gas activity results for carriers No. 1/HR1 and No. 2/HR2 and for the rest of the materials tested.

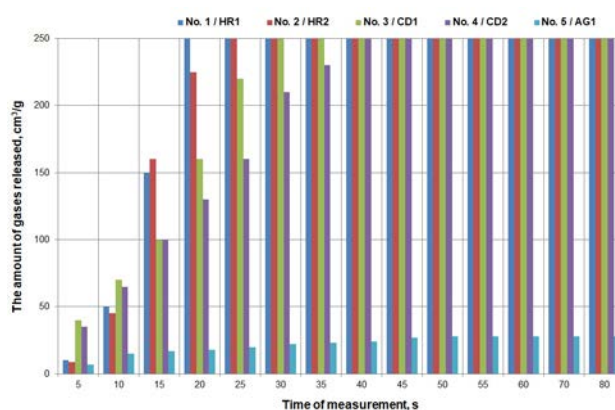


Fig. 2. Gas-forming tendency of carbonaceous additives as a lustrous carbon carriers examined at 1000°C

The observed gas emissions between 5th and 40th second of the measurement of tested additive types: a pair of CD, a pair of HR and an amorphous graphite (AG) are related to their chemical structure and its decomposition in high temperature (to the i.e. CO₂, CO, water) which were confirmed by resin-like [26,27,28], coal [10,29,30] and graphite [31] material studies. The identified differences in the chemical composition of individual LC carriers are related to the next stage of research in which the analysis of BTEX compounds was performed.

Table 3 summarizes the test results obtained for the released compounds from the BTEX group converted to 1 gram sample of the carbonaceous additive. As a result of the research it was found (Table 3) that the highest emission of harmful compounds was accompanying the heating process of samples with hydrocarbon resins, and the lowest - the heating process of sample No. 5/AG1 with amorphous graphite. Attention deserves the relatively low emission of BTEX compounds during testing of sample No. 3/CD1, where the lustrous carbon carrier was coal dust. During testing, the adopted measurement methodology (MDL/MQL) did not reveal the presence of BTEX compounds emitted from carrier No. 5/AG1. Moreover, the measuring device did not reveal any release of ethylbenzene from any of the five carbon carriers tested.

Table 3.

Mass [mg] of compounds from the BTEX group formed during heating of samples (32 mg) converted to 1 gram sample

Designation	B	T	E	X	Sum [mg]
No. 1/HR1	109	33	<MDL	10.7	152
No. 2/HR2	116	30	<MDL	8.2	154
No. 3/CD1	9.3	1.9	<MDL	<MQL	11,3
No. 4/CD2	12.8	12.8	<MQL	2.3	28
No. 5/AG1	<MDL	<MDL	<MDL	<MDL	<MDL
B – Benzene, T- Toluene, E – Ethylbenzene, X – Xylene					
MDL	0.19	0.15	0.15	0.12	
MQL	0.57	0.45	0.45	0.48	
MDL - Method Detection Limit					
MQL - Method Quantification Limit					

The materials after the high-temperature pyrolysis formed during measurements of the volatile matter content (875°C) were used for further qualitative and quantitative analyses of the products of the pyrolysis of carbonaceous additives. Similarly, the residues from the loss on ignition test (LOI) carried out at 950°C were analysed for their elemental composition.

Figures 3–7 show the SEM images of the sample material after pyrolysis carried out at 875°C. The SEM image of the carbonaceous additives exposed to the effect of high temperature was supplemented with the study of the elemental composition carried out by the energy dispersive X-ray spectrometry (EDX). The spectra show the quantitative and qualitative composition of the pyrolysis products taking into account the distribution of individual elements in the tested preparations. Figures 3 and 4 summarize the EDX tests performed on hydrocarbon resins. Figures 5 and 6 show the results of testing the coal dusts, and Figure 7 – the amorphous graphite.

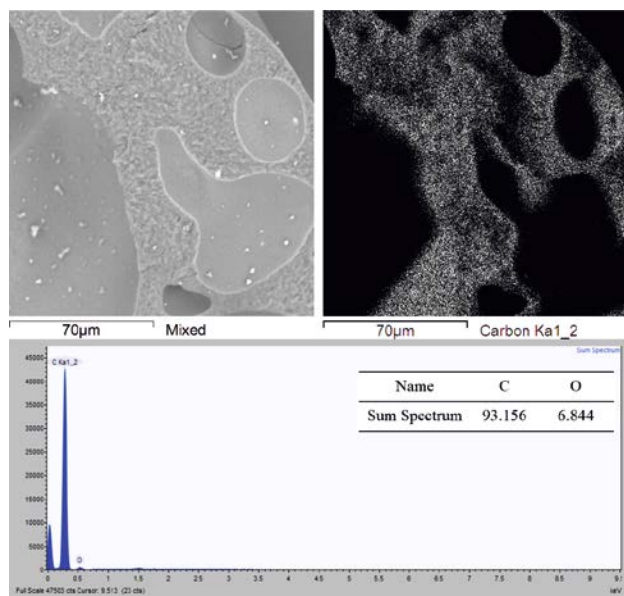


Fig. 3. Surface of lustrous carbon carrier No. 1/HR1 after pyrolysis. EDS/EDX spectra of measurements of the intensity of the occurrence of elements, data in % by weight

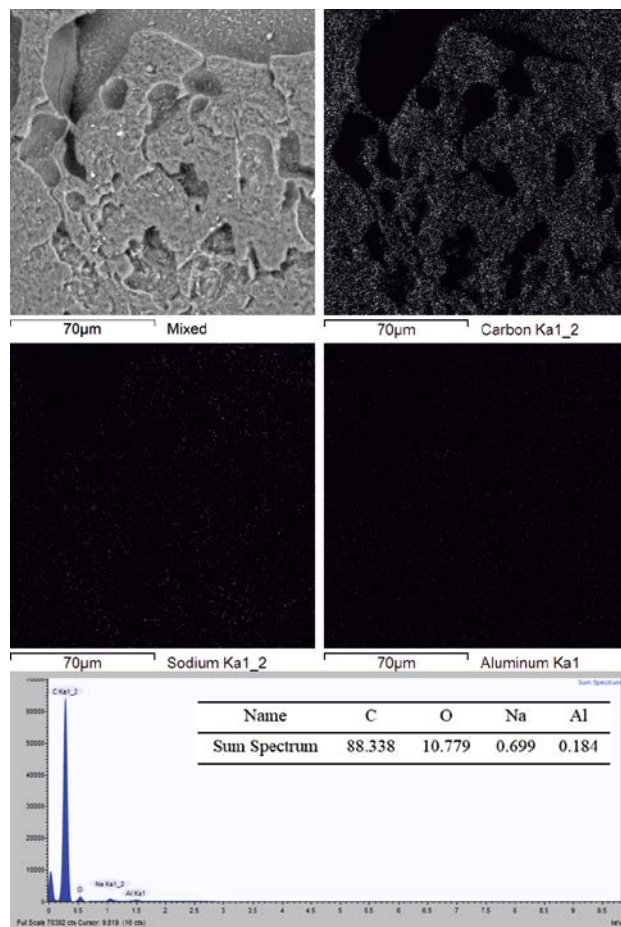


Fig. 4. Surface of lustrous carbon carrier No. 2/HR2 after pyrolysis. EDS/EDX spectra of measurements of the intensity of the occurrence of elements, data in % by weight

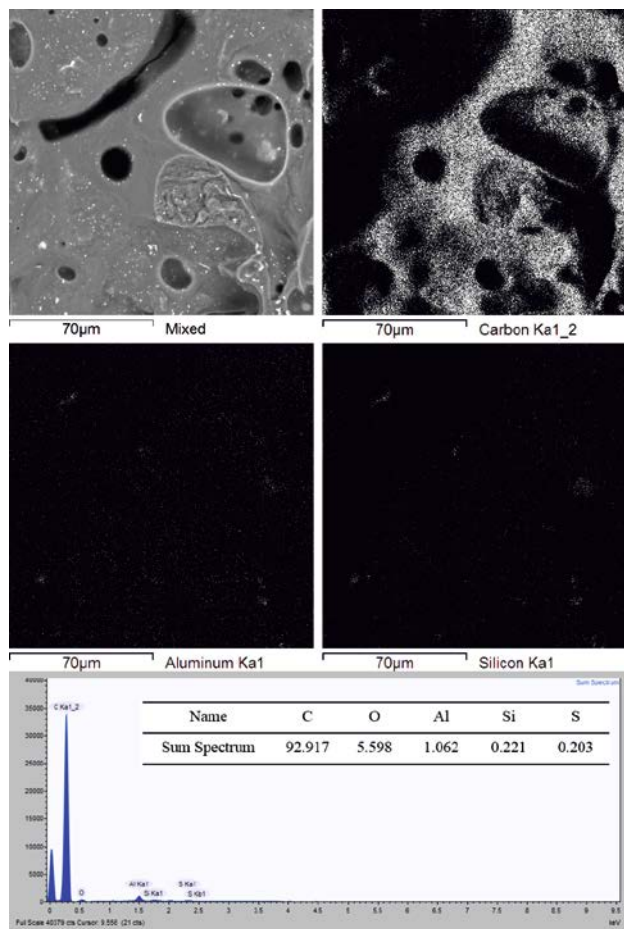


Fig. 5. Surface of lustrous carbon carrier No. 3/CD1 after pyrolysis. EDS/EDX spectra of measurements of the intensity of the occurrence of elements, data in % by weight

The resin pyrolysis products (Figs. 4-5) contain mainly C and small amounts of other elements such as Na and Al (No. 2/HR2). In the case of coal dust (Figs. 5-6), C also dominates the composition. The research also revealed other elements, i.e. Al and Si, present in the weight fraction of over 1%. In carriers No. 3 and No. 4, a small, i.e. not exceeding 1% by weight, fraction of S and Fe was also found. In the case of carrier No. 5/AG, the following elements were found in the post-pyrolysis product: Al, Si, and a small fraction of K and Fe (<1 wt.%).

The next stage of the research focused on the analysis of products formed during LOI tests carried out at 950°C in an oxidizing atmosphere. As a result of the LOI test carried out on carriers No. 1 and No. 2, the preparations were completely gasified (Table 2). On the remaining preparations, it was possible to determine the elemental composition after gasification of the organic additives (Table 4).

The analysis of carbon fractions in Table 4 showed complete thermal decomposition of additives No. 3/CD1 and No. 4/CD2, and partial decomposition in the case of amorphous graphite No. 5. In the case of coal dusts CD1 and CD2, the composition was dominated by the oxidation products with a significant fraction of elements: Al, Si, Ca and Fe. Last two of found in significant

amount: Ca and Fe are undesirable elements occurring i.e. in oxidised compounds (CaCO_3 and Fe_2O_3), which are identified as a responsible for lowering the sintering temperature of high-silica sand matrix. The EDS/EDX analysis disclosed the presence of products after thermal decomposition in oxidation atmosphere containing alkaline elements such as: K, Na and Mg, which amount in green moulding sand will increase with subsequent refresh cycles.

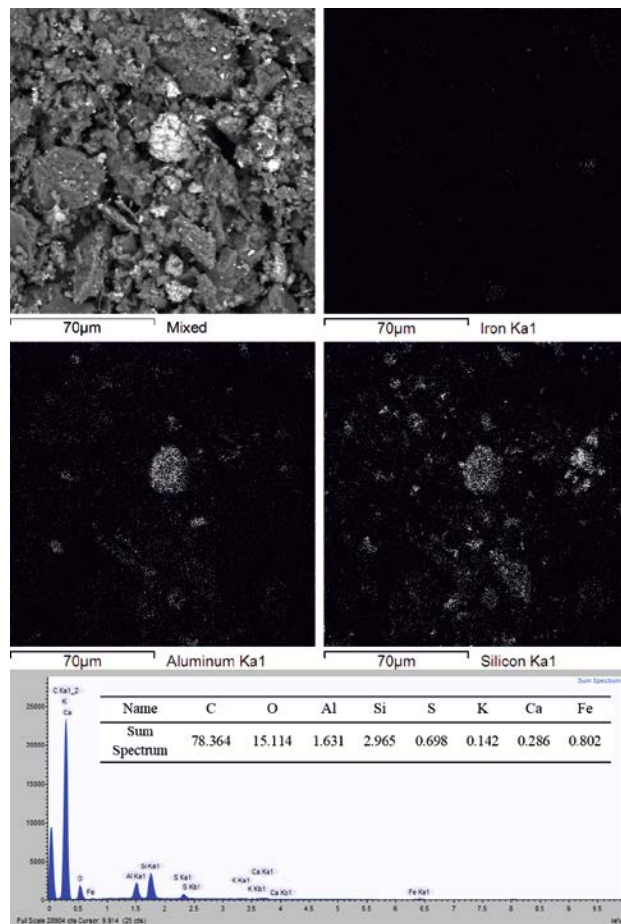


Fig. 6. Surface of lustrous carbon carrier No. 4/CD2 after pyrolysis. EDS/EDX spectra of measurements of the intensity of the occurrence of elements, data in % by weight

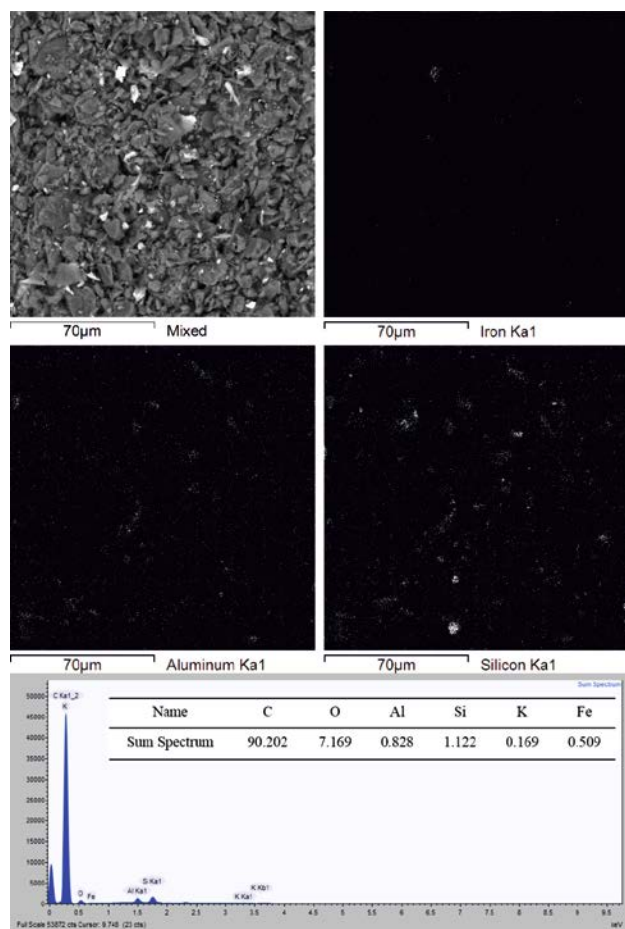


Fig. 7. Surface of lustrous carbon carrier No. 5/AG1 after pyrolysis. EDS/EDX spectra of measurements of the intensity of the occurrence of elements, data in % by weight

Table 4.
List of elements occurring in lustrous carbon carriers after LOI tests [% by weight]

Element:	No. 3/CD1	No. 4/CD2	No. 5/AG1
C	2.645	0.365	65.077
O	51.193	55.063	23.966
Na	1.944	0.355	0.124
Mg	0.648	0.516	0.326
Al	14.269	10.396	2.642
Si	13.200	22.096	4.507
P	1.502	0.159	-
S	0.726	1.050	-
K	0.819	0.718	0.706
Ca	5.905	3.402	0.548
Ti	0.987	0.515	0.162
Fe	6.162	5.364	1.941

4. Conclusions

The comparison of products resulting from the high-temperature pyrolysis of carbonaceous additives, which are carriers of lustrous carbon, leads to the following conclusions:

1. The introduction of common additives in the form of hydrocarbon resins (HR1 and HR2) to moulding sands improves their capability of the lustrous carbon coating formation. This advantage enables reducing the content of these additives when designing the composition of classic moulding sands. Moreover, gasification of these additives leaves no unnecessary products of their combustion in the sand. The amount of the released BTEX compounds calculated per 1 gram of the hydrocarbon resin addition is from several to several dozen times higher than it is in the case of other tested lustrous carbon carriers.

2. The types of coal dust selected for studies differ in the LC index, and additive No. 3/CD1 shows an above-average value of this index. The performed tests can be useful in designing the optimum composition of the green moulding sand reducing the amount of carbonaceous additives with the high LC content, facilitating its subsequent refreshing. The differences in the composition of the products of the pyrolysis and gasification of examined coal dusts depend on the bed which the tested green sand additives come from.

3. The amorphous graphite (AG1) selected for the tests is characterized by the lowest LC index. However, compared to other four lustrous carbon carriers, increasing the amount of this carrier added to the sand leaves the gas-forming tendency and the harmful effect caused by the release of BTEX compounds unchanged, and does not contaminate the sand with elements that may result in lowering the sintering temperature of high-silica sand matrix in moulding sand system.

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